

## PHYS393 – Statistical Physics

### Part 4: The Fermi-Dirac Distribution

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The story so far...

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In the previous parts of this course, we derived the Boltzmann distribution:

$$n_j = \frac{N}{Z} e^{-\frac{\varepsilon_j}{kT}}. \quad (1)$$

We applied this distribution to three example systems: a spin- $\frac{1}{2}$  magnetic solid, a collection of 1-dimensional quantum harmonic oscillators, and the Maxwell-Boltzmann gas. We saw how to derive a number of properties of these systems, including the energy, heat capacity, and entropy as functions of temperature.

We derived the Boltzmann distribution using a number of assumptions, including:

- the states formed by interchanging two particles with different energies represent *distinct* microstates;
- there is no restriction on the number of particles that can occupy a given single-particle state.

In quantum systems, these assumptions are not necessarily satisfied. In fact, we saw already in the case of the “rotational” heat capacity of diatomic hydrogen that constraints on the wave functions of the atomic nuclei led to observable effects: these constraints are not accounted in the above assumptions.

This suggests that to obtain a more complete and accurate description of the thermal properties of materials, we need to take a more careful look at the quantum properties of the constituent particles.

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## Indistinguishable particles

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We shall begin by re-visiting our assumption that interchanging the energies of two particles leads to distinct microstates. In other words, instead of assuming that the particles can be distinguished from each other, we shall make the assumption that the particles are indistinguishable. This is a more realistic assumption in many cases, and results in a fundamental change in the number of microstates accessible to a system.

Along the way, we shall find that there are two distinct cases, depending on whether single particle states can be occupied by at most one, or an unlimited number of particles.

The final result will be two new distributions for describing systems composed of indistinguishable particles. However, we will obtain the familiar Boltzmann distribution in the “classical” limit.

Consider a system with two single-particle states  $A$  and  $B$ . Let  $\psi_A(x)$  be the wave function for a particle in state  $A$ , and  $\psi_B(x)$  be the wave function for a particle in state  $B$ . Now suppose that the system contains two particles. If the interaction between the particles is very weak, then we can ignore any (small) change in the states  $A$  and  $B$ . If one particle occupies state  $A$ , and another particle occupies state  $B$ , then an approximate solution to the Schrödinger equation for the complete system is:

$$\psi(x_1, x_2) = \psi_A(x_1)\psi_B(x_2), \quad (2)$$

where  $x_1$  and  $x_2$  are the coordinates of particle 1 and particle 2, respectively.

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Symmetric and antisymmetric wave functions

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If we interchange the two particles, then we form a new wave function:

$$\psi'(x_1, x_2) = \psi_B(x_1)\psi_A(x_2). \quad (3)$$

However, if the particles are indistinguishable, then the properties of the system must be unchanged if the particles are interchanged. Assuming that the phase of the wave function is not observable, then  $\psi'$  can differ from  $\psi$  by (at most) some phase factor.

In other words:

$$\psi'(x_1, x_2) = e^{i\delta}\psi(x_1, x_2), \quad (4)$$

where  $\delta$  is a constant.

Thus, the operation of interchanging two particles is represented by multiplying the wave function by a phase factor,  $e^{i\delta}$ . However, if we interchange the particles *twice*, we get back to the exact situation we started with. This implies that:

$$e^{2i\delta} = 1, \quad (5)$$

and hence:

$$e^{i\delta} = \pm 1. \quad (6)$$

Both cases  $e^{i\delta} = +1$  and  $e^{i\delta} = -1$  are realised in nature: in the first case, we say that the wave function is *symmetric* with respect to the interchange of two particles; in the second case, we say that the wave function is *antisymmetric*. Note that the wave function only need be symmetric or antisymmetric if the two particles are indistinguishable.

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Symmetric and antisymmetric wave functions

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To enforce symmetry or antisymmetry, we need to modify the wave function (2). A symmetric wave function can be written:

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_A(x_1)\psi_B(x_2) + \psi_A(x_2)\psi_B(x_1)], \quad (7)$$

and an antisymmetric wave function can be written:

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_A(x_1)\psi_B(x_2) - \psi_A(x_2)\psi_B(x_1)]. \quad (8)$$

The factor  $1/\sqrt{2}$  is required for normalisation of the wave function:

$$\int |\psi(x_1, x_2)|^2 dx_1 dx_2 = 1. \quad (9)$$

Note that we assume that the states  $A$  and  $B$  are orthonormal:

$$\int |\psi_A(x)|^2 dx = 1, \quad \int \psi_A^*(x)\psi_B(x) dx = 0. \quad (10)$$

Particles for which the wave function is antisymmetric under interchange of any two of the particles are called *fermions*.

Particles for which the wave function is symmetric under interchange of any two of the particles are called *bosons*.

It can be shown, from quantum field theory, that particles with half-integer spin are always fermions, whereas particles with integer spin are always bosons.

In this part of the lecture course, we shall consider the statistical mechanics of fermions. We shall consider the statistical mechanics of bosons in the next part of the lecture course.

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### The Pauli exclusion principle

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Regarding fermions, our first observation is that antisymmetry of the wave function implies that each single-particle state cannot be occupied by the two particles at the same time. If we try to put two particles into state  $A$ , for example, the wave function becomes:

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_A(x_1)\psi_A(x_2) - \psi_A(x_2)\psi_A(x_1)] = 0. \quad (11)$$

The wave function vanishes.

This implies that for fermions, any single-particle state can be occupied by at most one particle: this is the Pauli exclusion principle.

With just two particles, it is easy to write down a symmetric or antisymmetric wave function. With more particles occupying more states, the wave function must be either symmetric or antisymmetric with respect to the interchange of *any* two particles.

The symmetry or antisymmetry can be enforced by writing the wave function as the determinant of a matrix, whose components are formed from all combinations of particles and states.

For example, with three *fermions* (with coordinates  $x_1$ ,  $x_2$  and  $x_3$ ) occupying three single-particle states ( $A$ ,  $B$  and  $C$ ), the wave function would be:

$$\psi(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_A(x_1) & \psi_A(x_2) & \psi_A(x_3) \\ \psi_B(x_1) & \psi_B(x_2) & \psi_B(x_3) \\ \psi_C(x_1) & \psi_C(x_2) & \psi_C(x_3) \end{vmatrix}. \quad (12)$$

The corresponding (symmetric) wave function for a system of bosons would be constructed in the same way, but each minus sign in the evaluation of the determinant must be replaced by a plus sign.

Recall that we derived the Boltzmann distribution by looking for the distribution that contained the largest number of microstates. To do this, we needed to write down an expression for the number of microstates in any given distribution.

$$t = \frac{N!}{n_1! n_2! n_3! \dots} \quad (13)$$

A distribution is specified by giving the number of particles occupying each single-particle state. The number of distinct microstates corresponding to a given distribution depends on whether the particles are distinguishable or indistinguishable; and, in the latter case, on whether the particles are fermions or bosons. Thus, there will be different distributions in the case of indistinguishable particles (Maxwell-Boltzmann distribution); fermions (Fermi-Dirac distribution); and bosons (Bose-Einstein distribution).

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### Distributions for fermions

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Let us consider states corresponding to energy levels  $\varepsilon_i$ . Each energy level can be degenerate; i.e. there can be many distinct single-particle states with the same energy. Let the number of states with energy  $\varepsilon_i$  be  $g_i$ ; and the number of particles with that energy be  $n_i$ . For fermions, it follows from the Pauli exclusion principle that the *largest* number of particles with energy  $\varepsilon_i$  is  $g_i$ , i.e. the maximum value of  $n_i$  is  $g_i$ .

The number of distinct ways of filling  $g_i$  single-particle states with  $n_i$  particles, with at most one particle per single-particle state, is:

$$t_i = \frac{g_i!}{n_i! (g_i - n_i)!}. \quad (14)$$

(Recall that  $m$  objects can be arranged in a sequence in  $m!$  different ways).

Each group of  $g_i$  states contributes a factor  $t_i$  to the total number of microstates for a given distribution  $\{n_i\}$ . Thus, the total number of microstates for fermions is:

$$t_F(\{n_i\}) = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!}. \quad (15)$$

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### Most probable distribution for fermions

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Using the principle of equal a priori probabilities, the most likely distribution in which to find a system of a large number of fermions is that with the largest number of microstates. Therefore, we need to maximise  $t_F$ , or equivalently,  $\ln t_F$ , with respect to small changes in the energy level populations  $n_i$ .

From (15), we have:

$$\ln t_F = \sum_i \ln \left( \frac{g_i!}{n_i! (g_i - n_i)!} \right). \quad (16)$$

Assuming that  $g_i$  and  $n_i$  are large so that we can use Stirling's approximation, we have:

$$\ln t_F \approx \sum_i [g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i)]. \quad (17)$$

The change in  $\ln t_F$  with respect to changes  $dn_i$  in the populations  $n_i$  is:

$$d(\ln t_F) \approx \sum_i \ln \left( \frac{g_i - n_i}{n_i} \right) dn_i. \quad (18)$$



Changes in the populations of the single-particle states are subject to the constraints:

$$\sum_i n_i = N, \quad \therefore \quad \sum_i dn_i = 0, \quad (19)$$

and:

$$\sum_i n_i \varepsilon_i = U, \quad \therefore \quad \sum_i \varepsilon_i dn_i = 0, \quad (20)$$

where  $N$  is the total number of particles in the system, and  $U$  is the total energy, both of which are constant.

Combining equation (18) with (19) and (20), with Lagrange multipliers  $\alpha$  and  $\beta$ , we have:

$$d(\ln t_F) \approx \sum_i \left[ \ln \left( \frac{g_i - n_i}{n_i} \right) + \alpha + \beta \varepsilon_i \right] dn_i = 0. \quad (21)$$

Equation (21):

$$d(\ln t_F) \approx \sum_i \left[ \ln \left( \frac{g_i - n_i}{n_i} \right) + \alpha + \beta \varepsilon_i \right] dn_i = 0,$$

must be true for any set of variations  $dn_i$ ; therefore, we can write:

$$\ln \left( \frac{g_i - n_i}{n_i} \right) + \alpha + \beta \varepsilon_i = 0. \quad (22)$$

Solving equation (22), we find that the populations of the energy levels  $\varepsilon_i$  in the most probable distribution are:

$$n_i = \frac{g_i}{e^{-\alpha - \beta \varepsilon_i} + 1}. \quad (23)$$

Writing:

$$e^{-\alpha} = B, \quad \text{and} \quad \beta = -\frac{1}{kT}, \quad (24)$$

where  $k$  is Boltzmann's constant, the most probable distribution for fermions (23) can be written:

$$n_i = \frac{g_i}{B e^{\frac{\varepsilon_i}{kT}} + 1}. \quad (25)$$

This is the Fermi-Dirac distribution. The constant  $B$  can be found from the normalisation condition:

$$\sum_i n_i = \sum_i \frac{g_i}{B e^{\frac{\varepsilon_i}{kT}} + 1} = N. \quad (26)$$

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### The Fermi-Dirac distribution for a dilute system

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At first sight, the Fermi-Dirac distribution looks quite different from the Maxwell-Boltzmann distribution, which we derived under the assumption that the particles were distinguishable. But consider the case that the population of each energy level is much less than the number of available states at that energy:

$$\frac{n_i}{g_i} \ll 1. \quad (27)$$

In this case, we have from (25):

$$B e^{\frac{\varepsilon_i}{kT}} + 1 \gg 1, \quad (28)$$

and therefore:

$$B e^{\frac{\varepsilon_i}{kT}} + 1 \approx B e^{\frac{\varepsilon_i}{kT}}. \quad (29)$$

The Fermi-Dirac distribution can then be approximated by:

$$n_i \approx \frac{g_i}{B} e^{-\frac{\varepsilon_i}{kT}}, \quad (30)$$

which has the same form as the Maxwell-Boltzmann distribution.

We see that for a “dilute” system, in which the population of each energy level is much less than the number of states available at that energy level, the Maxwell-Boltzmann distribution provides a good approximation to the more accurate Fermi-Dirac distribution.

We expect to see the Fermi-Dirac distribution differ significantly from the Maxwell-Boltzmann distribution under conditions in which the population of some of the energy levels approaches the number of states available at those energy levels. This can occur at low temperature, as we now show.

We begin by defining a parameter  $\mu$ , with units of energy, such that  $B = e^{-\mu/kT}$ . The Fermi-Dirac distribution is then written:

$$n_i = \frac{g_i}{e^{\frac{\varepsilon_i - \mu}{kT}} + 1}. \quad (31)$$

Now consider the probability that a particular single-particle state is occupied by a fermion. Since, at energy  $\varepsilon_i$ , there are  $n_i$  particles distributed over  $g_i$  single-particle states, the probability that a particular state is occupied is:

$$\frac{n_i}{g_i} = \frac{1}{e^{\frac{\varepsilon_i - \mu}{kT}} + 1}. \quad (32)$$

Now consider the low temperature limit,  $T \rightarrow 0$ . We see that in this limit,

$$\frac{n_i}{g_i} = 1 \quad \text{for} \quad \varepsilon_i < \mu, \quad (33)$$

and:

$$\frac{n_i}{g_i} = 0 \quad \text{for} \quad \varepsilon_i > \mu. \quad (34)$$

In other words, in the low temperature limit, all states with energy below  $\mu$  are occupied, and none of the states with energy above  $\mu$  are occupied.

The parameter  $\mu$  is called the chemical potential. In general, the chemical potential will be a function of the variables specifying the macrostate, including the number of particles, and the temperature.

The chemical potential in the Fermi-Dirac distribution plays a similar role to the partition function  $Z$  in the Boltzmann distribution. It is determined by the normalisation condition; depends on the temperature; and parameterises the distribution.

For the Boltzmann distribution, we found that knowledge of the partition function was very useful for deriving thermal properties of the system. The chemical potential is similarly useful in systems of fermions.

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### The chemical potential

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As an example, consider the case that  $g_i$  is constant. The normalisation condition can be written:

$$\sum_i n_i \approx \int_0^\infty \frac{g d\varepsilon}{e^{\frac{\varepsilon-\mu}{kT}} + 1} = N, \quad (35)$$

where there are  $g d\varepsilon$  single-particle states in the (small) energy range from  $\varepsilon$  to  $\varepsilon + d\varepsilon$ .

Hence, we find that the chemical potential is given by:

$$\mu(T) = kT \ln \left( e^{\frac{N}{gkT}} - 1 \right). \quad (36)$$

As we might expect, the low temperature limit is:

$$\mu(T) \rightarrow \frac{N}{g} \quad \text{as} \quad T \rightarrow 0. \quad (37)$$

In the low temperature limit, the  $N$  lowest energy states are occupied by particles; since the states are uniformly distributed in energy, the energy of the highest-energy occupied state is  $N/g$ .

Now we define the *Fermi temperature*  $T_F$  by:

$$T_F = \frac{\mu(0)}{k} \quad (38)$$

where  $\mu(0)$  is the value of the chemical potential  $\mu(T)$  in the limit  $T \rightarrow 0$ , and  $k$  is Boltzmann's constant.  $\mu(0)$  is sometimes called the Fermi energy, and written  $\varepsilon_F$ . The Fermi energy is related to the Fermi temperature by:

$$\varepsilon_F = kT_F. \quad (39)$$

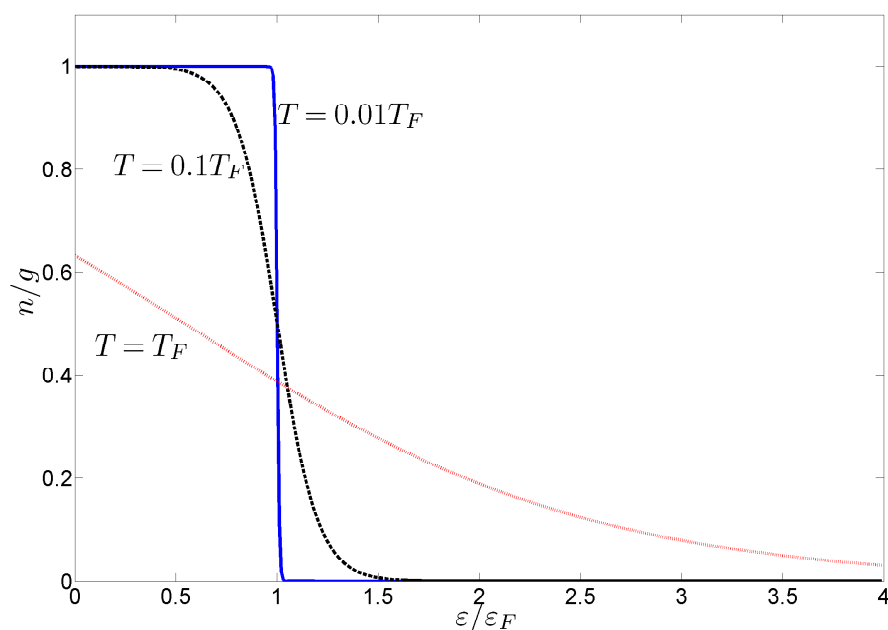
Let us plot  $n/g$  (the fraction of occupied single-particle states) as a function of energy for various temperatures; the result is shown on the next slide. We see that for:

$$T \ll T_F, \quad (40)$$

the distribution is significantly different from a Maxwell-Boltzmann exponential decay; while for:

$$T \gg T_F, \quad (41)$$

the distribution starts to approach a Maxwell-Boltzmann distribution.



Note: this is the special case, where the density of states  $g$  is constant.

Note that for  $\varepsilon = \mu$ , we find:

$$\frac{n_i}{g_i} = \frac{1}{e^{\frac{\varepsilon - \mu}{kT}} + 1} = \frac{1}{2}. \quad (42)$$

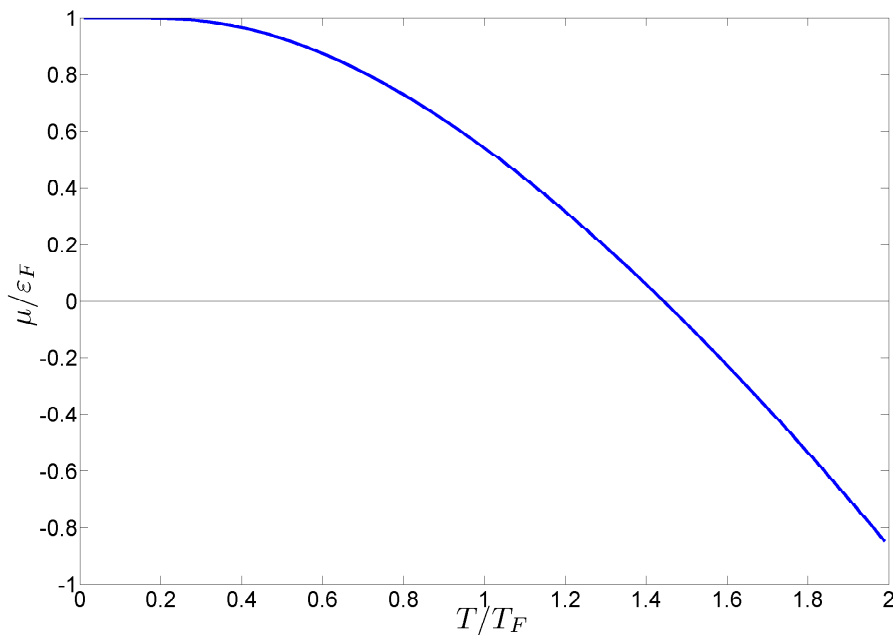
At an energy level equal to the chemical potential, the average population of the available states is 1/2. This is a general result for the Fermi-Dirac distribution; it is not restricted to the case where the density of states is constant.

It is often useful to know how the chemical potential varies with temperature. In the case where the density of states is constant, the chemical potential is given by (36):

$$\mu(T) = kT \ln \left( e^{\frac{N}{gkT}} - 1 \right).$$

We plot  $\mu(T)$  as a function of temperature  $T$  on the next slide; the significant feature is that at low temperatures ( $T$  less than about  $T_F/2$ ), the chemical potential is almost constant: it varies very little with temperature.

Note that as the temperature increases, the chemical potential  $\mu(T)$  becomes negative. We saw from equation (42) that states with energy equal to the chemical potential have an average population of 1/2. Thus, when the chemical potential becomes negative, *all* states have an average population less than 1/2.



Note: this is the special case, where the density of states  $g$  is constant.

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## The Fermi gas

Let us work through an example more thoroughly. Since we are going to invest some time and effort, we might as well choose an example with some physical significance. An appropriate example is provided by the *Fermi gas*: this is the fermion equivalent of the Maxwell-Boltzmann gas. A Fermi gas consists of a collection of weakly-interacting fermions that are free to move within a bounded volume  $V$ , but are unable to move beyond the boundary.

Fermi gases occur in a number of physical situations, including:

- conduction electrons in a metal;
- liquid  $^3\text{He}$ ;
- neutron stars.

Let us first find the energy distribution of particles in the Fermi gas. At high temperatures, this will approach the energy distribution of particles in the Maxwell-Boltzmann gas; but at low temperatures, we expect the fermion nature of the particles to be important.

The energy distribution of particles in a Fermi gas is given by:

$$n(\varepsilon) d\varepsilon = g(\varepsilon) f(\varepsilon) d\varepsilon, \quad (43)$$

where  $f(\varepsilon)$  is the *Fermi function*:

$$f(\varepsilon) = \frac{1}{e^{\frac{\varepsilon - \mu}{kT}} + 1}, \quad (44)$$

and  $g(\varepsilon)$  is the density of states, given in this case by:

$$g(\varepsilon) d\varepsilon = (2s + 1) \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\varepsilon} d\varepsilon, \quad (45)$$

where  $s$  is the spin of the particles in the gas.

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### The Fermi gas: chemical potential

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To find an explicit expression for the energy distribution  $n(\varepsilon)$ , we need to find an expression for the chemical potential  $\mu$  in terms of the temperature,  $T$ . The chemical potential  $\mu$  is determined by the normalisation:

$$\int_0^\infty n(\varepsilon) d\varepsilon = N. \quad (46)$$

Thus, to find an expression for the chemical potential  $\mu$ , we need to solve:

$$(2s + 1) \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\frac{\varepsilon - \mu}{kT}} + 1} d\varepsilon = N. \quad (47)$$

This is not an easy integral to perform, so we resort to some “tricks”, as we now proceed to explain.

To simplify things (slightly) we shall consider the specific case of particles with spin  $s = \frac{1}{2}$ .



To perform the integral (47), we first consider an integral of the form:

$$I = \int_0^\infty \frac{dG(\varepsilon)}{d\varepsilon} f(\varepsilon) d\varepsilon. \quad (48)$$

Performing this integral by parts gives:

$$I = -G(0) - \int_0^\infty G(\varepsilon) \frac{df(\varepsilon)}{d\varepsilon} d\varepsilon. \quad (49)$$

Now we use the fact that, for temperatures  $T \ll T_F$ , the Fermi function  $f(\varepsilon)$  is essentially a step function. Thus, the derivative vanishes everywhere, except at energies close to the chemical potential, where it becomes large: in fact, as the temperature tends to zero, the derivative of the Fermi function tends to the Dirac delta function.

Let us make the assumption that  $T \ll T_F$ . Then, because of the properties of  $df/d\varepsilon$ , only values of  $G(\varepsilon)$  for  $\varepsilon \approx \mu$  contribute to the integral  $I$ . That means we can expand  $G(\varepsilon)$  in a Taylor series around  $\varepsilon = \mu$ :

$$G(\varepsilon) = G(\mu) + (\varepsilon - \mu)G'(\mu) + \frac{1}{2}(\varepsilon - \mu)^2 G''(\mu) + \dots \quad (50)$$

Substituting this series into equation (49) gives:

$$I = -G(0) + G(\mu)I_0 + kT G'(\mu)I_1 + \frac{(kT)^2}{2} G''(\mu)I_2 + \dots \quad (51)$$

where:

$$I_\ell = - \int_0^\infty \left( \frac{\varepsilon - \mu}{kT} \right)^\ell \frac{df}{d\varepsilon} d\varepsilon. \quad (52)$$

Now we use:

$$\frac{df}{d\varepsilon} = -\frac{e^{\frac{\varepsilon-\mu}{kT}}}{\left(e^{\frac{\varepsilon-\mu}{kT}} + 1\right)^2 kT}, \quad (53)$$

to give:

$$I_\ell \approx \int_{-\infty}^{\infty} x^\ell \frac{e^x}{(e^x + 1)^2} dx. \quad (54)$$

We have again made use of the fact that the integrand is large only over a narrow range, this time to extend the lower limit of the integration to  $-\infty$ , and change the variable of integration.

We can look up the values of  $I_\ell$  for  $\ell = 0, 1, 2, \dots$ . We find:

$$I = -G(0) + G(\mu) + \frac{\pi^2}{6}(kT)^2 G''(\mu) + \dots \quad (55)$$

If we choose:

$$G(\varepsilon) = \frac{2}{3}\varepsilon^{\frac{3}{2}}, \quad (56)$$

so that:

$$G'(\varepsilon) = \varepsilon^{\frac{1}{2}}, \quad \text{and} \quad G''(\varepsilon) = \frac{1}{2}\varepsilon^{-\frac{1}{2}}, \quad (57)$$

then, applying the result (55) to equation (47), we find:

$$\frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\frac{\varepsilon-\mu}{kT}} + 1} d\varepsilon \approx \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \left(\frac{2}{3}\mu^{\frac{3}{2}} + \frac{\pi^2}{12}(kT)^2 \mu^{-\frac{1}{2}}\right) \approx N. \quad (58)$$

The approximate solution to equation (58) is:

$$\mu \approx \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F}\right)^2\right], \quad (59)$$

where  $kT_F = \varepsilon_F$ , and the Fermi energy  $\varepsilon_F$  is given by:

$$\varepsilon_F = \lim_{T \rightarrow 0} \mu = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V}\right)^{\frac{2}{3}}. \quad (60)$$

We can check our result for the Fermi energy (60) by using the fact that in the low temperature limit, all single-particle states with energy below the Fermi energy  $\varepsilon_F$  are filled, and all single-particle states with energy above  $\mu_0$  are empty. Thus:

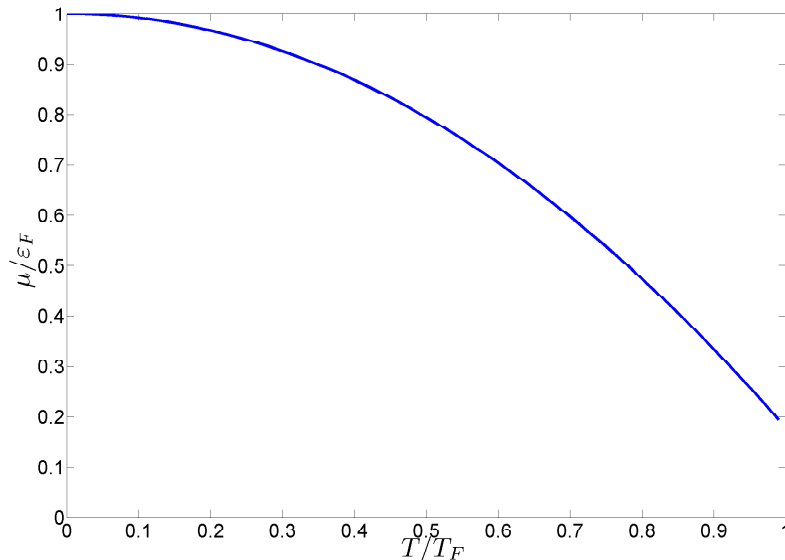
$$\int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon = N. \quad (61)$$

With the density of states  $g(\varepsilon)$  given by (45):

$$g(\varepsilon) d\varepsilon = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\varepsilon} d\varepsilon, \quad (62)$$

this gives the same result as in (60) above.

As in the case of a system with constant density of states, we find that for  $T \ll T_F$ , the chemical potential has a weak dependence on temperature (as before, we define  $kT_F = \varepsilon_F$ ):

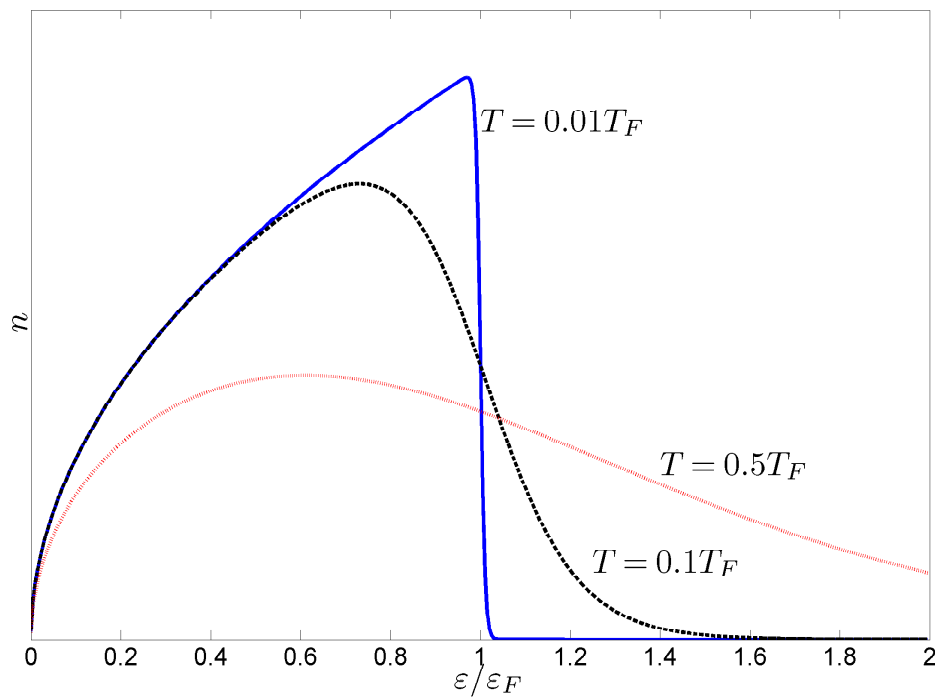


We have derived explicit expressions (59) and (60) for the chemical potential, valid for  $T \ll T_F$ :

$$\mu \approx \varepsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 \right], \quad \varepsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{\frac{2}{3}}.$$

The distribution of particles with energy in the Fermi gas can then be written:

$$n(\varepsilon) \approx \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{\sqrt{\varepsilon}}{e^{\frac{\varepsilon-\mu}{kT}} + 1}. \quad (63)$$



The total energy in the Fermi gas is given by:

$$U = \int_0^\infty \varepsilon n(\varepsilon) d\varepsilon. \quad (64)$$

Using equation (63) for the particle distribution  $n(\varepsilon)$ :

$$n(\varepsilon) d\varepsilon \approx \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{\sqrt{\varepsilon}}{e^{\frac{\varepsilon-\mu}{kT}} + 1} d\varepsilon,$$

we have:

$$U = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{\varepsilon^{\frac{3}{2}}}{e^{\frac{\varepsilon-\mu}{kT}} + 1} d\varepsilon. \quad (65)$$

The integral can be performed using the previous results, (48) and (55), with:

$$G(\varepsilon) = \frac{2}{5} \varepsilon^{\frac{5}{2}}. \quad (66)$$

The result for the total energy of the Fermi gas is:

$$U = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \left[ \frac{2}{5} \mu^{\frac{5}{2}} + \frac{\pi^2}{4} (kT)^2 \mu^{\frac{1}{2}} \right]. \quad (67)$$

Using equations (59) and (60):

$$\mu \approx \varepsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 \right], \quad \varepsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{\frac{2}{3}},$$

we can express the total energy as:

$$U = \frac{3}{5} N \varepsilon_F \left[ 1 + \frac{5\pi^2}{12} \left( \frac{T}{T_F} \right)^2 \right], \quad (68)$$

where, as usual,  $kT_F = \varepsilon_F$ , and the above results are valid for  $T \ll T_F$ .

We can see whether our result (68) for the total energy in a Fermi gas is sensible, by making a rough estimate as follows. First, we calculate the total energy in the limit  $T \rightarrow 0$ , by using the fact that in the low temperature limit, all energy levels up to the chemical potential  $\varepsilon_F$  are occupied, and all energy levels above the chemical potential are empty. The total energy in the limit  $T \rightarrow 0$  is then:

$$U_0 = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^{\varepsilon_F} \varepsilon^{\frac{3}{2}} d\varepsilon, \quad (69)$$

$$= \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{2}{5} \varepsilon_F^{\frac{5}{2}}, \quad (70)$$

$$= \frac{3}{5} N \varepsilon_F. \quad (71)$$

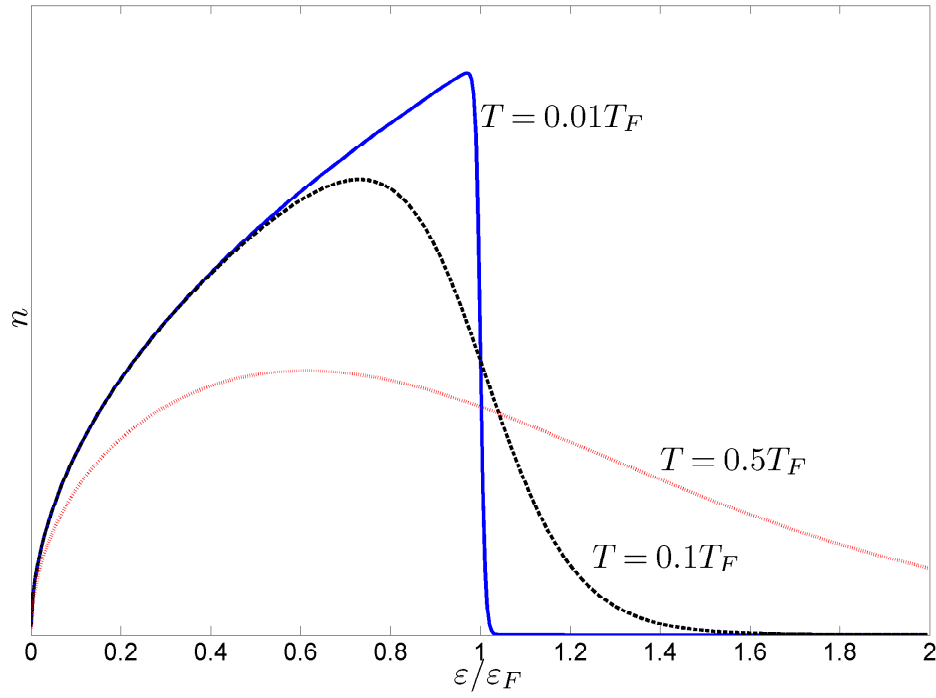
In the last line, we have used, from (60):

$$N = \frac{V}{3\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \varepsilon_F^{\frac{3}{2}}. \quad (72)$$

To estimate the temperature dependence of the total energy of the system is a little more difficult. Let us assume that:

1. at temperature  $T$ , particles within energy  $kT$  of the Fermi energy  $\varepsilon_F$  are excited into higher energy levels;
2. the particles excited into higher energy levels have an energy gain  $\frac{3}{2}kT$ .

The first assumption is justified by inspection of the plot showing the energy distribution of a Fermi gas at different temperatures (reproduced on the next slide). The second assumption is justified by the principle of equipartition of energy, with the further assumption that the particles have three degrees of freedom.



## The Fermi gas: total energy

The increase in energy at a temperature  $T$  ( $\ll T_F$ ) is therefore given approximately by:

$$\Delta U \approx g(\varepsilon_F)kT \cdot \frac{3}{2}kT. \quad (73)$$

$g(\varepsilon_F)$  is the density of states at the zero-point chemical potential  $\varepsilon_F$ . For a spin- $\frac{1}{2}$  Fermi gas, the density of states is given by (45):

$$g(\varepsilon) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}}. \quad (74)$$

Hence,

$$g(\varepsilon_F) = \frac{3N}{2\varepsilon_F}, \quad (75)$$

which gives:

$$\Delta U \approx \frac{9}{4}N\varepsilon_F \left( \frac{T}{T_F} \right)^2. \quad (76)$$

Hence, our estimate for the total energy in the Fermi gas is, for  $T \ll T_F$ :

$$U = U_0 + \Delta U \approx \frac{3}{5}N\varepsilon_F + \frac{9}{4}N\varepsilon_F \left(\frac{T}{T_F}\right)^2. \quad (77)$$

This agrees quite well with our more careful (but still approximate) result (68):

$$U = \frac{3}{5}N\varepsilon_F \left[ 1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F}\right)^2 \right] = \frac{3}{5}N\varepsilon_F + \frac{\pi^2}{4}N\varepsilon_F \left(\frac{T}{T_F}\right)^2.$$

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### The Fermi gas: zero-point energy

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As  $T \rightarrow 0$ , the total energy of the Fermi gas becomes:

$$U \rightarrow U_0 = \frac{3}{5}N\varepsilon_F = \frac{3}{5} \frac{\hbar^2}{2m} \left(\frac{3\pi^2}{V}\right)^{\frac{2}{3}} N^{\frac{5}{3}}. \quad (78)$$

This can be compared with the total energy of the Maxwell-Boltzmann gas in the same low temperature limit, which we found in a previous part of this course:

$$U_{0,\text{M-B}} = 3 \frac{\hbar^2}{2m} \left(\frac{\pi^3}{V}\right)^{\frac{2}{3}} N. \quad (79)$$

The most significant difference between these expressions is that the energy of the Fermi gas in the low temperature limit has an additional factor  $N^{\frac{2}{3}}$ . Since  $N$  can be large, the zero-temperature energy of the Fermi gas can be much larger than the corresponding Maxwell-Boltzmann gas. This is a direct consequence of the Pauli exclusion principle, which prevents the fermions in the Fermi gas from all falling into the single-particle state with the lowest energy. For particles in a Maxwell-Boltzmann gas, there is no such restriction.



From the temperature dependence of the total energy, we can easily find an expression for the heat capacity at constant volume:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{\pi^2}{2} N k \frac{T}{T_F}. \quad (80)$$

Again, this result is valid for  $T \ll T_F$ . It shows that at temperatures much less than the Fermi temperature, the heat capacity is proportional to the temperature, and vanishes in the limit  $T \rightarrow 0$ .

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The Fermi gas: example of conduction electrons

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We mentioned previously that the conduction electrons in a metal may be modelled as a Fermi gas. Let us apply the above results to find the Fermi temperature and heat capacity in a “typical” case. The Fermi temperature is important, because it tells us the range of temperatures for which the expressions we have derived are valid.

The Fermi temperature is given by:

$$T_F = \frac{\varepsilon_F}{k}, \quad \text{and} \quad \varepsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{\frac{2}{3}}. \quad (81)$$

Note that  $N/V$ , the number of electrons per unit volume, is given for a monovalent metal by:

$$\frac{N}{V} = \frac{\rho N_A}{A}, \quad (82)$$

where  $\rho$  is the density of the metal,  $N_A$  is Avogadro’s constant, and  $A$  is the relative atomic mass.

Let us consider the example of silver, which has one conduction electron per atom. Using the following data:

Density	$\rho$	$10,500 \text{ kg m}^{-3}$
Relative atomic mass	$A$	$0.108 \text{ kg mol}^{-1}$
Reduced Planck's constant	$\hbar$	$1.055 \times 10^{-34} \text{ J s}$
Electron mass	$m$	$9.11 \times 10^{-31} \text{ kg}$
Boltzmann's constant	$k$	$1.38 \times 10^{-23} \text{ J K}^{-1}$
Avogadro's number	$N_A$	$6.023 \times 10^{23} \text{ mol}^{-1}$

we find:

$$\varepsilon_F \approx 8.82 \times 10^{-19} \text{ J}, \quad (83)$$

and:

$$T_F = \frac{\varepsilon_F}{k} \approx 63,900 \text{ K}. \quad (84)$$

The Fermi temperature is very high by everyday standards; so at room temperatures, our expression for the heat capacity should work well.

At room temperature,  $T = 293 \text{ K} \ll T_F$ , we can use equation (80) for the heat capacity:

$$C_V = \frac{\pi^2}{2} N k \frac{T}{T_F}.$$

For 1 kg of silver, the number of electrons is  $N = N_A/A = 5.58 \times 10^{24}$ . Hence, at 293 K, we find that the specific heat capacity of the conduction electrons in silver is:

$$c_V \approx 1.74 \text{ J kg}^{-1} \text{ K}^{-1}. \quad (85)$$

This compares with the measured specific heat capacity (at constant pressure) of silver,  $235 \text{ J kg}^{-1} \text{ K}^{-1}$ . Clearly, if our model is correct, the conduction electrons make only a small contribution to the specific heat capacity.

Our conclusion is correct: in fact, conduction electrons in metals make only a small contribution to the heat capacity of the material. We shall consider the dominant contributions, from vibrations of atoms in the material, in the next part of this course.

However, as we shall see, the heat capacity associated with atomic vibrations varies as the cube of the temperature, whereas the heat capacity associated with the conduction electrons varies linearly with the temperature:

$$C_{V,m} = \gamma T + AT^3, \quad (86)$$

where the constant  $\gamma$  characterises the contribution to the heat capacity from the conduction electrons, the constant  $A$  (not the atomic mass!) characterises the contribution from atomic vibrations, and the subscript  $m$  denotes the heat capacity per mole.

This suggests that if we can achieve sufficiently low temperatures, the contribution from the conduction electrons can start to dominate.

The heat capacity per mole of the conduction electrons is, from equation (80), given by:

$$C_{V,m} = \frac{\pi^2}{2} N_A k \frac{T}{T_F}. \quad (87)$$

Hence,

$$\gamma = \lim_{T \rightarrow 0} \frac{\partial C_{V,m}}{\partial T} = \frac{\pi^2}{2} \frac{N_A k}{T_F}. \quad (88)$$

For silver, we find:

$$\gamma \approx 0.643 \text{ mJ mol}^{-1} \text{ K}^{-2}. \quad (89)$$

$\gamma$  is a measurable quantity. We can obtain  $\gamma$ , for example, as the intercept of a plot of  $C_{V,m}/T$  vs  $T$  (or  $T^2$ ). The agreement between theory and measurement is good, though not exact.

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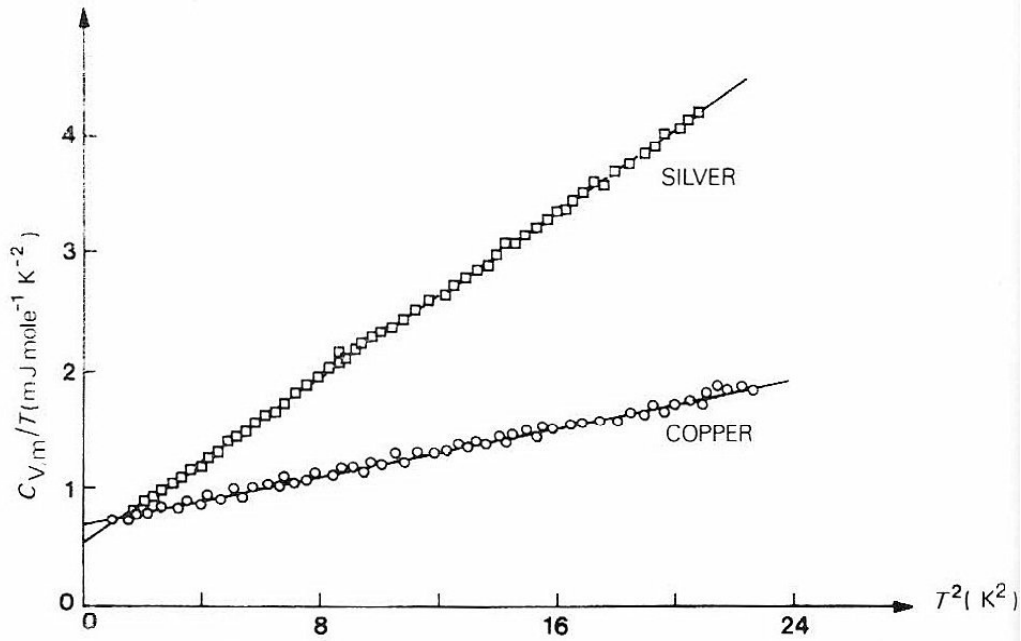


Figure 12.7—Low temperature molar heat capacity of metals;  $C_{V,m}/T$  is plotted against  $T^2$ . The results are consistent with equation (12.29), according to which  $C_{V,m}$  is equal to  $\gamma T + AT^3$ . The intercepts give the values of  $\gamma$ . The values of  $A$  can be determined from the slopes. (Reproduced with permission from *Statistical Mechanics and Properties of Matter* by E. S. R. Gopal, Ellis Horwood Ltd., Chichester.)

## The Fermi gas: equation of state

Finally for the Fermi gas, let us find the equation of state, which expresses the relationship between pressure, volume and temperature. We start from the first law of thermodynamics, in the form:

$$dU = T dS - p dV. \quad (90)$$

Thus, the pressure is given by:

$$p = - \left( \frac{\partial U}{\partial V} \right)_S. \quad (91)$$

The total energy is given by:

$$U = \sum_i n_i \varepsilon_i, \quad (92)$$

where  $n_i$  is the number of particles in a single-particle state with energy  $\varepsilon_i$ .

Now, since the number of accessible microstates depends on the populations of the states (see equation 15); and the entropy (by Boltzmann's equation) depends on the number of accessible microstates, the populations  $n_i$  are constant at constant entropy. Thus:

$$\left(\frac{\partial U}{\partial V}\right)_S = \sum_i n_i \frac{\partial \varepsilon_i}{\partial V}. \quad (93)$$

Recall that, for particles bounded in a box, the single-particle energy levels are related to the volume by:

$$\varepsilon_i \propto V^{-\frac{2}{3}}. \quad (94)$$

Hence,

$$\frac{d\varepsilon_i}{\varepsilon_i} = -\frac{2}{3} \frac{dV}{V}, \quad (95)$$

and so:

$$\frac{\partial \varepsilon_i}{\partial V} = -\frac{2}{3} \frac{\varepsilon_i}{V}. \quad (96)$$

Thus, summing over energy states, we obtain:

$$p = -\left(\frac{\partial U}{\partial V}\right)_S = \sum_i \frac{2}{3} n_i \frac{\varepsilon_i}{V} = \frac{2}{3} \frac{U}{V}. \quad (97)$$

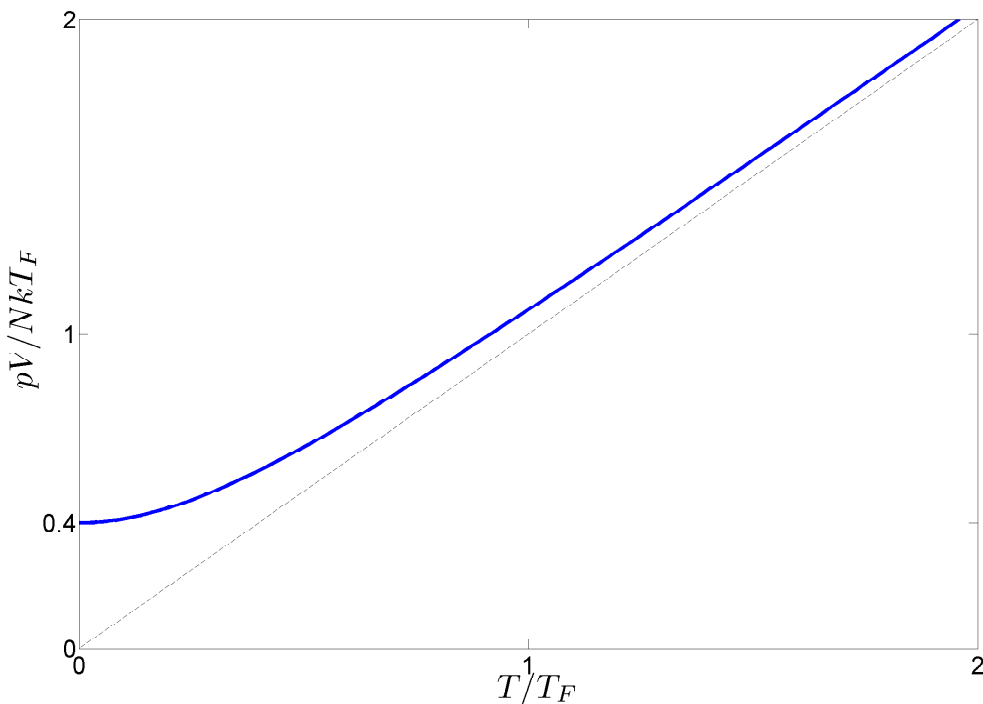
Using equation (68) for the total energy, we find:

$$pV = \frac{2}{5}N\varepsilon_F \left[ 1 + \frac{5\pi^2}{12} \left( \frac{T}{T_F} \right)^2 \right]. \quad (98)$$

This equation of state is valid in the regime  $T \ll T_F$ , and is quite different from that for a Maxwell-Boltzmann gas. There is a large pressure even in the limit  $T \rightarrow 0$ ; this corresponds to the large internal energy that exists in the system, even in the limit of low temperature.

For temperatures much larger than the Fermi temperature,  $T \gg T_F$ , the Fermi-Dirac distribution approaches the Maxwell-Boltzmann distribution, and the equation of state tends towards that of the ideal gas:

$$pV = NkT. \quad (99)$$



Finally, we consider the effect of an external magnetic field on the conduction electrons in a metal. We again assume that the conduction electrons can be modelled as a Fermi gas. Since electrons have a magnetic moment:

$$\mu_B = \frac{e\hbar}{2m}, \quad (100)$$

the immediate effect of an external magnetic field is to change the energy of the spin states:

$$\Delta\varepsilon = \pm\mu_B B, \quad (101)$$

where the energy of the state increases if the spin associated with that state is opposite to the magnetic field, and decreases if the spin is parallel to the magnetic field.

For simplicity, let us consider the limit  $T \rightarrow 0$ . Since, in practice, we find that  $T \ll T_F$  at everyday temperatures, this is likely to be a reasonable approximation in commonplace situations.

The reason for taking the limit  $T \rightarrow 0$  is that in the low temperature limit, we know that energy states up to the Fermi energy are occupied, and states above this energy are unoccupied.

The external magnetic field changes increases the energy of states with spin opposite to the field, and decreases the energy of states with spin parallel to the field. Therefore, to maintain full occupancy of states up to the Fermi energy, the number of particles with spin opposite to the field must be different from the number of particles with spin parallel to the field.

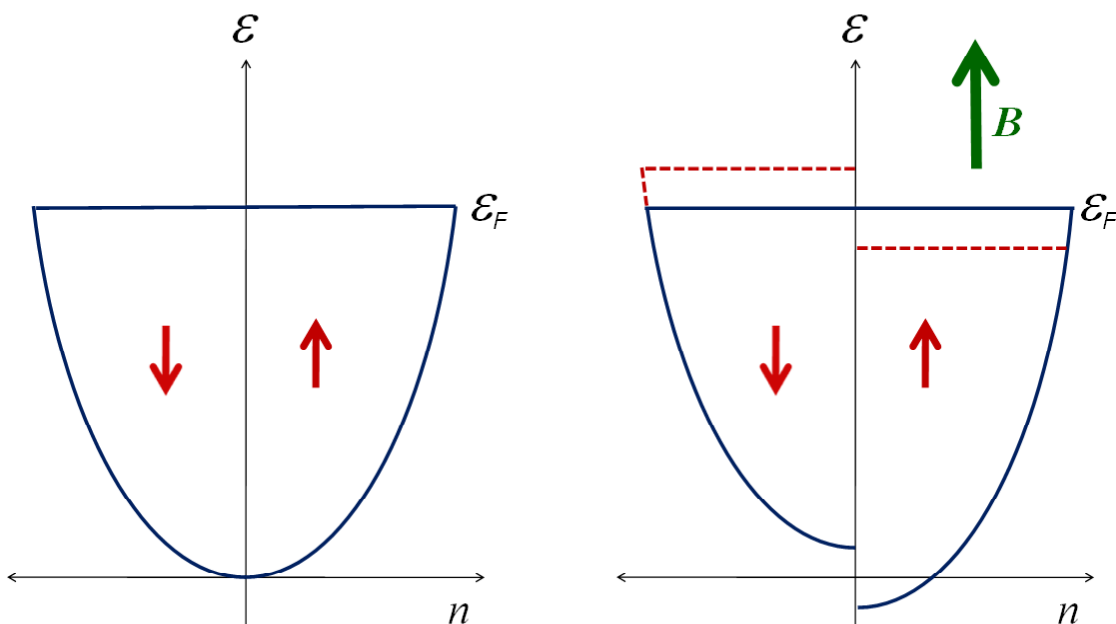
The total magnetic moment per unit volume of the conduction electrons in a material is given by:

$$M = (n_{\uparrow} - n_{\downarrow}) \mu_B \quad (102)$$

where  $n_{\uparrow}$  and  $n_{\downarrow}$  are, respectively, the number of electrons per unit volume with spin parallel to the external magnetic field, and the number of electrons per unit volume with spin opposite to the external magnetic field.

When the external field is applied, a number of electrons with spin opposite to the field will “flip” to have spin parallel to the field; this maintains a uniform occupation of states up to the Fermi energy.

The number of electrons that flip their spins is approximately  $\frac{1}{2}g(\varepsilon_F) \cdot \mu_B B$ , where  $g(\varepsilon) d\varepsilon$  is the number of states in the small energy range  $\varepsilon$  to  $\varepsilon + d\varepsilon$ .





Therefore, in the presence of the magnetic field, there will be a difference in the number of electrons with spin parallel to the field and spin opposite to the field:

$$n_{\uparrow} - n_{\downarrow} = 2 \times \frac{1}{2V} g(\varepsilon_F) \cdot \mu_B B. \quad (103)$$

Hence, the material acquires a magnetisation (magnetic moment per unit volume):

$$M = \frac{1}{V} g(\varepsilon_F) \cdot \mu_B B \cdot \mu_B. \quad (104)$$

Using the density of states (75):

$$g(\varepsilon_F) = \frac{3N}{2\varepsilon_F} \quad (105)$$

the magnetisation is:

$$M = \frac{3N}{2V\varepsilon_F} \cdot \mu_B^2 B. \quad (106)$$

The magnetisation is related to the external magnetic field by the magnetic susceptibility  $\chi_m$ :

$$M = \chi_m H, \quad (107)$$

and

$$B = \mu H, \quad (108)$$

where  $\mu$  is the magnetic permeability. Assuming  $\chi_m \ll 1$ ,

$$B = \mu_0(1 + \chi_m)H \approx \mu_0 H, \quad (109)$$

where  $\mu_0$  is the permeability of free space. Hence, the susceptibility can be written:

$$\chi_m \approx \mu_0 \frac{M}{B} = \frac{3}{2} \mu_0 \frac{N}{V\varepsilon_F} \mu_B^2. \quad (110)$$

Let us consider aluminium as an example. Aluminium has three electrons in its outer shell; we shall assume that two electrons have their spins paired, so only a single electron per atom contributes to the magnetic properties of the material. We shall further assume that the electrons contributing to the magnetic properties can be treated as a Fermi gas.

We shall use the following properties of aluminium:

Density	$\rho$	$2,710 \text{ kg m}^{-3}$
Relative atomic mass	$A$	$0.0270 \text{ kg mol}^{-1}$

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The number of electrons per unit volume is then:

$$\frac{N}{V} = \rho \frac{N_A}{A} = 6.28 \times 10^{28} \text{ m}^{-3}, \quad (111)$$

and the Fermi energy is:

$$\varepsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{\frac{2}{3}} = 9.24 \times 10^{-19} \text{ J}. \quad (112)$$

Then, using (110), we find for the susceptibility:

$$\chi_m \approx 1.1 \times 10^{-5}. \quad (113)$$

This compares with the measured value:

$$\chi_m \approx 2.2 \times 10^{-5}. \quad (114)$$

The agreement is not great – we are out by a factor of two. But magnetism is a complicated phenomenon, and at least we got the right order of magnitude...

You should be able to:

- Explain that the wave function for a system of fermions must be antisymmetric under exchange of any two particles; and show that this leads to the Pauli exclusion principle.
- Derive the Fermi-Dirac distribution, as the most probable distribution for a system of particles in which a maximum of one particle can occupy any single-particle state.
- Show that, for a *dilute* system, the Fermi-Dirac distribution can be approximated by the Maxwell-Boltzmann distribution.
- Define, and explain the physical significance of: the chemical potential; the Fermi energy; and the Fermi temperature.
- Derive an approximate expression for the chemical potential of a Fermi gas, including the temperature dependence to second order.
- Sketch the energy distribution for particles in a Fermi gas, showing how the distribution changes with temperature (up to the Fermi temperature).
- Derive expressions for the total energy and the heat capacity of a Fermi gas.
- Derive the equation of state for a Fermi gas at temperatures small compared to the Fermi temperature.
- Derive an expression for the magnetic susceptibility of a material whose magnetic properties are dominated by a Fermi gas of electrons.